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Bureau of Mines Report of Investigations/1974

Coal Mine Combustion Products

**Neoprenes, Polyvinyl Chloride Compositions,
Urethane Foam, and Wood**

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Coal Mine Combustion Products

Neoprenes, Polyvinyl Chloride Compositions, Urethane Foam, and Wood

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BUREAU OF MINES

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The work upon which this report is based was done for the Bureau of Mines, U.S. Department of the Interior, by Ultrasystems, Inc., under Contract No. H0133004.

This publication has been cataloged as follows:

Hartstein, Arthur M

Coal mine combustion products: neoprenes, polyvinyl chloride compositions, urethane foam, and wood, by Arthur M. Hartstein and David R. Forshey. [Washington] U.S. Bureau of Mines [1974]

25 p. illus., tables. (U.S. Bureau of Mines. Report of investigations 7977)

Based on work done for the Bureau of Mines, U.S. Dept. of the Interior, by Ultrasystems, Inc., under Contract No. HO133004.

1. Coal mines and mining. 2. Mine fires. 3. Mine gases. 4. Rubber, Artificial. 5. Urethane foam. 6. Wood. I. U.S. Bureau of Mines. II. Forshey, David R., jt. auth. III. Ultrasystems, Inc. IV. Title. (Series)

TN23.U7 no. 7977 622.06173
U.S. Dept. of the Int. Library

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COAL MINE COMBUSTION PRODUCTS

Neoprenes, Polyvinyl Chloride Compositions, Urethane Foam, and Wood

by

Arthur M. Hartstein¹ and David R. Forshey²

ABSTRACT

The Bureau of Mines through contract with Ultrasystems, Inc., obtained gram per gram data of products formed on thermal oxidative degradation of selected compositions, both under dynamic and static conditions. Four broad classes of materials were studied: Polyvinyl chloride compositions, neoprene compositions, rigid urethane foams, and variously treated woods. Whenever possible, comparisons between pure components and composites were attempted. Thermogravimetric and differential thermal analyses were performed to gain understanding of the processes occurring and to explore the feasibility of using these analyses as a method of material identification. The toxic products detected and quantitated included HCl, H₂S, CO, SO₂, CS₂, COS, HCOOH, CH₃COOH, formaldehyde, acrolein, C₆H₆, chloroprene, chloroethanol, benzyl chloride, aniline, and furfural.

INTRODUCTION

Investigations performed by Ultrasystems, Inc., under a previous contract,³ revealed the inherent danger of toxic product formation associated with the use underground of a number of materials. This study was aimed at determining on a gram per gram basis the products obtained on thermal oxidative degradation of selected groups of materials both under static and dynamic conditions. Relatively moderate temperatures were employed to assess the danger of overheating due to malfunction of equipment or circuitry rather than to study the effect of actual combustion.

Polyvinyl chloride-based and neoprene-based compositions are used extensively underground. The same applies to wood since it is the main material of

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³Paciorek, K. L., R. H. Kratzer, and J. Kaufman. Coal Mine Combustion Products Identification and Analysis. BuMines Open File Rept. 1-73, 1972, 158 pp.; available for consultation at Bureau of Mines libraries in Denver, Colo., Pittsburgh, Pa., Spokane, Wash., and Twin Cities, Minn., and at the Central Library, U.S. Department of the Interior, Washington, D.C.; and from National Technical Information Service, Springfield, Va., PB 214 124.

construction in coal mines and metal and nonmetal mines. Thus, the thermal oxidative behavior of these materials is of great importance to mine safety. Rigid foams are being utilized more and more underground as dust control and ground stabilization agents. In the case of woods, the effect of the various treatments necessary to render the wood flame retardant and rot resistant is of major importance.

It is believed that only by knowing what to expect when a certain material is subjected to heat (be it under dynamic or static environment) can disaster preventive measures be developed. These will most likely involve design and material distribution aspects as well as material selection and improvement approaches.

EXPERIMENTAL WORK

The detailed data are given in Ultrasystems' report⁴ generated under this program. For the dynamic environment investigations, a modified stagnation burner arrangement was employed. This instrument and its operation are described adequately in the previous report of investigations.⁵ Thus, these details are not given here. The main change in this work is that under the current program, to allow the trapping of the total product, all the ports were closed except the one outlet that led to the trapping arrangement. The trapping arrangement was composed of a trap cooled to minus 78° C and two traps cooled to minus 196° C. The trapping is sufficiently effective to condense practically all the air that passed through and is 100 pct effective so far as condensable products are concerned. Figure 1 shows the top view of the modified stagnation burner. The sample is introduced through port W, which is then immediately closed with the window. The connection, or bypass T, was introduced to avoid the perturbation of the laminar flow. In figure 2 is given the schematic drawing of the stagnation zone. In a typical experiment, a weighed material sample was heated in the stagnation zone for 15 min. At the conclusion of the test, the sample residue is withdrawn and weighed. The traps are then evacuated while cooled at minus 196° C. The liquid nitrogen condensibles are then fractionated through room temperatures minus 23°, minus 78°, into minus 196° C trap. Each of the fractions is measured and weighed and subjected (both as vapor and liquid) to gas chromatography, infrared, mass spectrometry, and wet analysis (Cl^- , CN^- , and NH_4^+). For the gas chromatographic analysis, an 8-foot by 1/8-inch-diam Porapak Q⁶ column is employed programmed from 50° to 220° C at 8° C/min using a thermal conductivity detector and 36 ml/min helium flow.

⁴ Paciorek, K. L., R. H. Kratzer, J. Kaufman, and J. H. Nakahara. Coal Mine Combustion Products Identification and Analysis. BuMines Open File Rept. 8-74, 1973, 158 pp.; available for consultation at Bureau of Mines libraries in Pittsburgh, Pa., Twin Cities, Minn., Denver, Colo., and Spokane, Wash., and at the Central Library, U.S. Department of the Interior, Washington, D.C.; and from National Technical Information Service, Springfield, Va., PB 226 994/AS.

⁵ Hartstein, A. M., and D. R. Forshey. Coal Mine Combustion Products: Identification and Analysis. BuMines RI 7872, 1974, 12 pp.

⁶ Reference to trade names does not imply endorsement by the Bureau of Mines.

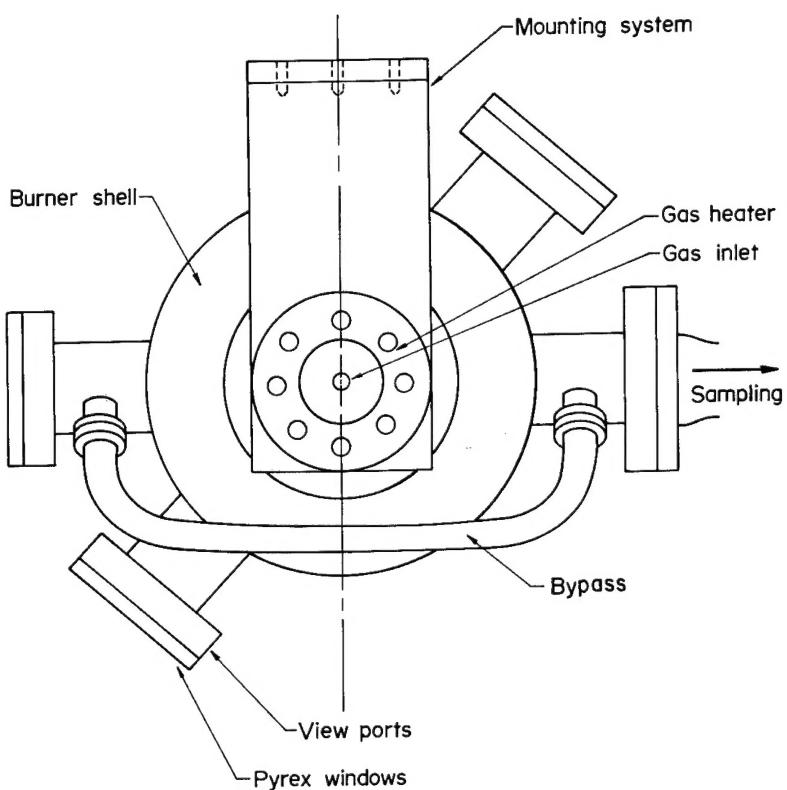


FIGURE 1. - Top view of stagnation burner with mounting system.

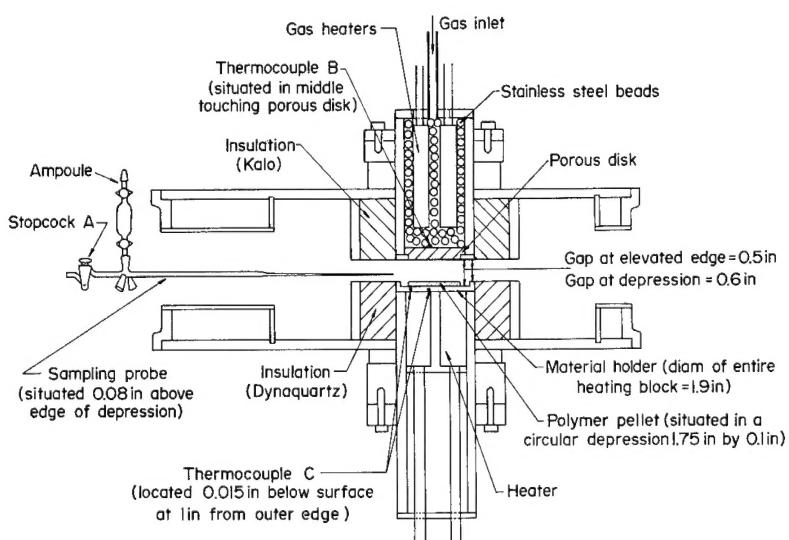


FIGURE 2. - Detailed drawing of stagnation zone with gas, block, and auxiliary heaters and sample pan.

The sealed system consists essentially of a 2-liter bulb equipped with a fingerlike protrusion. The diagram of the arrangement is presented in figure 3. For a given experiment, the weighed sample is placed in the finger, and the bulb is then evacuated. Subsequently the bulb is filled with air to the desired pressure (below atmospheric) and stopcock A closed. Thermal decomposition is accomplished by putting preheated metal bath around the finger and heating for 30 min. After removal of the metal bath, the system is allowed to cool to room temperature, and the pressure is measured by opening stopcock A to the previously evacuated calibrated volume, which includes trap 1. Knowing this value, the pressure in the volume V_1 is calculated. The noncondensibles are then collected in the Sprengel pump, and the minus 196° C condensibles are retained in traps 1 and 2, which are cooled at this stage with liquid nitrogen. The noncondensibles are analyzed by mass spectrometry (for CO, CH₄, and oxygen depletion), and the condensibles are fractionated in the same manner as was described for the stagnation burner investigations.

Certain aspects should be clarified in this section:

1. The amount of hydrogen chloride found in the sealed system is always higher than in the stagnation

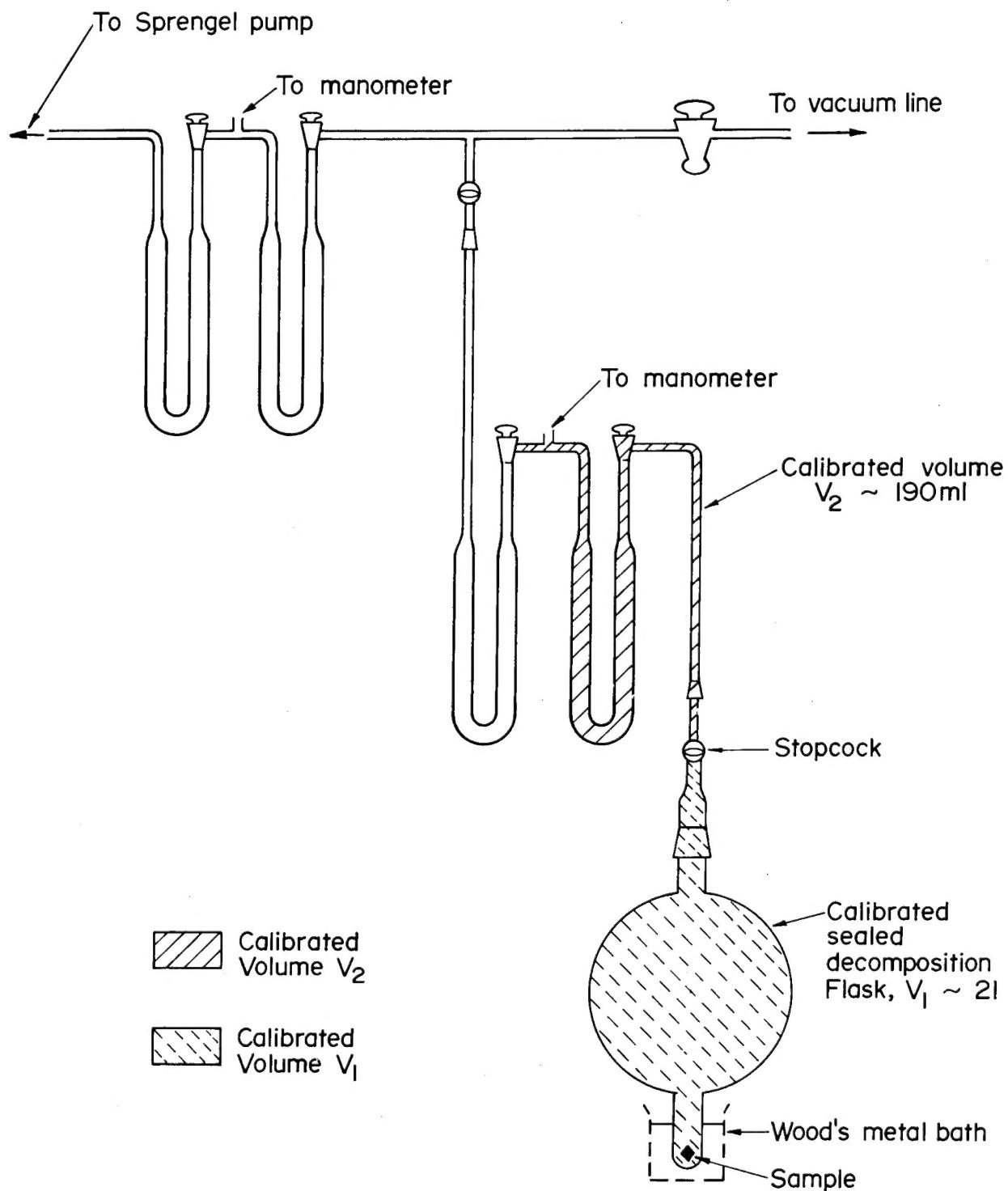


FIGURE 3. - Sealed system for thermal oxidative degradations.

burner presumably due to the interaction of hydrogen chloride with the large metal surfaces present in the stagnation apparatus.

2. The values given for compounds such as acrolein, formaldehyde, and to a certain degree, formic acid, are felt to be much lower than their actual amounts. In some instances, lack of product detection does not mean that no product was formed. This lack of detection is due to strong retention of these products in water and tars and their apparent tendency to associate during condensation, which results in a greatly decreased volatility. Study of these low volatility components will alleviate this problem.

RESULTS AND DISCUSSION

Nineteen compositions comprising four broad families of materials, namely, neoprenes, polyvinyl chlorides, urethane foams, and variously treated pine samples, were subjected to thermal oxidative degradations. The list of the materials studied is given in table 1, and the experimental details of the tests performed are summarized for the static system in table 2 and for the dynamic system in table 3. The experiments were primarily conducted to determine the products formed on the gram per gram basis with special emphasis on the toxic constituents. These results are given in tables 4-10, inclusive. In addition to the tests performed in the sealed system and stagnation burner, each of the materials was subjected to thermogravimetric analysis (TGA) to assess the thermal behavior, to correlate decomposition phases with a given product evolution, and to evaluate the potential application of TGA to material identification. The TGA identification of materials was of particular interest insofar as neoprenes and PVC (polyvinyl chloride) based compositions are concerned in view of their chlorine content. In the case of wood (pine samples), both TGA and differential thermal analysis (DTA) were performed to determine the action of a specific additive or treatment upon decomposition mechanism. This was of particular importance in the case of wood treated with fire retardant since the treatment is directed at altering the decomposition mechanisms. Selected TGA curves are presented in figures 4-13, inclusive. As a reference for each series of materials, the "pure" constituent, that is, neoprene gum, polyvinyl chloride "virgin resin," or untreated wood, was investigated. In addition to articles actually used in the mines, a number of "model" cured and/or treated compositions were studied to gain some understanding of the effect of specific ingredients. This was mainly accomplished in the case of neoprenes and the woods. To facilitate the presentation of the pertinent findings of this study, each group of materials will be discussed separately.

TABEL 1.- List of materials investigated¹

Material	Origin	Material description
Uncured neoprene.....	Air Force Materials Laboratory.	Neoprene gum, WRT (Du Pont product).
Cured neoprene.....do.....	Neoprene gum, WRT (Du Pont product) cured as denoted in table 5.
Neoprene composition 4A.	Bureau of Mines.....	Manufactured by United States Steel Corp. (labeled D0500W).
Neoprene composition 3A.do.....	Hose conduit No. 1949; composed of neoprene polymer reinforced with polyester; manufactured by H. K. Porter, Thermoid Div.
Polyvinyl chloride pure resin.	Air Force Materials Laboratory.	Polyvinyl chloride resin; manufactured by United States Rubber Co.; pressed into pellets.
Polyvinyl chloride, nylon composition 6A.	Bureau of Mines.....	Brattice cloth No. 1800Y composed of nylon scrim laminated with thin PVC layer; manufactured by C. R. Daniels.
Polyvinyl chloride composition 7A.do.....	O'Koseal 200 type THW or MTW; composed of PVC; manufactured by O'Konite Cable (subsidiary of LTV).
Polyvinyl chloride, nylon composition 13Ado.....	Reinforced plastic fabric rip-proof No. 75 clear III, nylon-reinforced PVC; manufactured by Griffolyn Co., Inc.
Polyvinyl chloride, nylon composition 9B.	Manufacturer.....	No. 3 nylon (Glasstex) (composition: PVC-antimony trioxide ?); Johnston-Morehouse-Dickey Co.
Polyvinyl chloride composition 10B.do.....	No. 4 plastic 15Y (appearance: solid yellow plastic; composition: PVC-antimony trioxide ?) manufactured by Johnston-Morehouse-Dickey Co.
Polyurethane rigid foam system, composition 1B.do.....	Resin component--CCl ₃ F 22 pct; polyols, amines, catalyst 78 pct. Activator component--CCl ₃ F 5 pct, isocyanate polymeric, MDI type 94 pct; manufactured by Callery Chemical Co.
Polyurethane rigid foam system, composition 2B.do.....	Same as preceding.
Polyurethane rigid foam system, composition 16A.	Bureau of Mines.....	Urethane-isocyanurate No. 4 foam; manufactured by Callery Chemical Co.

See footnote at end of table.

TABLE 1. - List of materials investigated¹--Continued

Material	Origin	Material description
Untreated pine sample 1D.	Bureau of Mines.....	Standard southern yellow pine.
Untreated pine sample 6Ddo.....	Do.
Treated pine sample 2D.do.....	Standard southern yellow pine treated with oil-borne preservative (pentachlorophenol); 0.37 lb ft ⁻³ ; impregnation by Koppers Co.
Treated pine sample 3D.do.....	Standard southern yellow pine treated with creosote (coal tar distillate); 10.6 lb ft ⁻³ ; impregnation by Koppers Co.
Treated pine sample 4D.do.....	Standard southern yellow pine treated with fire retardant type C, Minalith $(\text{NH}_4)_2\text{HPO}_4$, 10 pct; $(\text{NH}_4)_2\text{SO}_4$, 60 pct; $\text{Na}_2\text{B}_4\text{O}_7$, 10 pct; H_3BO_3 , 20 pct; 0.4 lb ft ⁻³ ; impregnation by Koppers Co.
Treated pine sample 5D.do.....	Standard southern yellow pine treated with waterborne preservative-CCA (CrO_3 , CuO , As_2O_5); 0.40 lb ft ⁻³ ; impregnation by Koppers Co.

¹Some of the materials listed, namely, those denoted by letters A and B, have been subjected to some testing previously. The letter identification has been continued in this report to facilitate cross referencing.

TABLE 2. - Experimental data for sealed tube degradations of the compositions studied

Sample identification ¹	Tube P, ml	Initial P, mm	Final P, mm	React. temp, °C	Sample wt, mg	Residue		Oxygen consumed		Total product	
						mg	Pct ²	mg	Pct ³	mg ⁴	Pct ⁵
Neoprene, uncured..	2,047	505.6	542.1	368	582	244	42.0	30.6	8.4	281.2	76.3
Neoprene, cured....	2,045	559.1	570.0	371	278	168	60.3	53.5	13.1	122.3	74.6
Neoprene 4A.....	2,047	580.0	592.9	366	278	176	63.4	61.1	14.3	104.8	64.3
Neoprene 3A.....	2,045	495.3	500.2	372	506	361	71.4	42.4	11.5	73.5	39.3
PVC resin.....	2,047	503.3	585.3	368	611	201	32.9	46.1	12.3	402.1	88.1
PVC 6A.....	2,047	507.1	529.9	370	637	243	38.1	35.9	9.5	187.9	43.7
PVC 13A.....	2,045	495.8	548.9	369	628	231	36.8	25.4	4.0	267.8	63.4
PVC 7A.....	2,047	505.2	548.9	368	632	224	35.4	16.1	4.3	282.8	66.7
PVC 9B.....	2,045	507.1	540.2	371	625	188	30.1	52.2	14.2	328.1	67.1
PVC 10B.....	2,045	511.7	559.9	375	640	250	39.2	52.9	14.0	311.9	70.5
Urethane 1B.....	2,047	510.8	523.9	365	287	32	11.3	10.8	2.9	126.0	47.4
Urethane 2B.....	2,047	507.2	524.5	370	272	50	18.2	12.5	3.3	113.5	48.3
Urethane 16A.....	2,045	502.9	505.9	370	276	148	53.5	64.6	17.4	122.2	63.4
Wood 1D.....	2,047	504.8	536.6	370	615	208	33.8	48.0	12.9	342.3	75.2
Wood 6D.....	2,045	505.3	536.1	371	597	203	34.0	35.5	9.5	290.0	67.6
Wood 2D.....	2,045	506.8	538.1	368	625	206	32.9	43.2	11.6	280.3	60.6
Wood 3D.....	2,047	506.6	532.0	370	630	207	32.8	33.3	9.0	263.0	57.7
Wood 4D.....	2,045	504.8	530.1	371	603	283	47.0	54.0	14.7	297.0	79.4
Wood 5D.....	2,045	501.2	528.8	370	605	212	35.0	49.0	13.3	321.6	72.8

¹Material identification is given in table 1.

²Percent of the weight of the starting material. This is only the solid removable portion of the residue and does not include the tars and oils deposited on the side of the tube.

³Percent of oxygen available.

⁴Includes the HCl found in the residue and in the bottom of the reaction flask.

⁵Percent of the total products expected based on sample weight loss and oxygen consumed.

TABLE 3. - Summary of experimental data for stagnation burner degradations of the compositions studied

Sample identification ¹	Gas temp, °C	Block temp, °C	Glow, min	Sample wt, mg	Residue		Condensable volatiles		Room temp involatiles	
					mg	Pct ²	mg	Pct ²	mg	Pct ²
Neoprene, uncured..	401	395	No glow	963	357	37.1	504.9	52.4	174.3	18.1
Neoprene, cured....	403	404	2-15	930	76	8.2	1,458.4	156.9	189.2	20.3
Neoprene 4A.....	406	396	4-15	931	141	15.2	1,219.1	131.2	206.6	22.2
Neoprene 3A.....	402	393	No glow	1,009	618	61.3	243.0	24.1	93.6	9.3
PVC resin.....	398	394	No glow	968	344	35.5	744.0	76.9	64.6	6.7
PVC 6A.....	406	394	No glow	1,035	373	36.0	475.3	45.9	192.2	18.6
PVC 13A.....	407	402	No glow	1,038	363	34.9	550.4	53.0	159.2	15.3
PVC 7A.....	407	402	No glow	1,230	433	35.2	401.6	32.7	174.4	14.2
PVC 9B.....	403	401	No glow	1,002	265	26.5	329	32.8	209.2	20.9
Wood 1D.....	401	397	8-15	1,020	132	12.9	904.9	88.8	147.6	14.5
Wood 2D.....	401	397	6-15	1,007	34	3.4	797.9	79.2	202.2	20.1
Wood 3D.....	406	404	No glow	1,008	264	26.2	630.2	62.5	116.2	11.5
Wood 4D.....	399	400	No glow	1,018	404	39.7	982.7	96.5	17.0	1.7
Wood 5D.....	410	404	4-6	1,003	14	1.4	1,220.3	121.6	144.0	14.4

¹Material identification is given in table 1.

²Percent of the weight of the starting material.

TABLE 4. - Products of neoprene compositions¹
(sealed tube studies)

Product	Uncured, mg/g	Cured, mg/g	4A, mg/g	3A, mg/g
CO.....	13.2	6.19	19.1	7.35
CH ₄	2.15	1.04	.72	1.16
HCl.....	311.9	200.0	109.8	64.7
CO ₂	16.1	104.4	137.5	26.6
SO ₂	-	.54	.32	.69
COS.....	-	-	-	.03
CS ₂	-	.84	.50	2.12
H ₂ S.....	-	.11	.22	.31
C _x H _y ²	3.52	3.38	4.35	2.27
C ₆ H ₆	1.41	.25	.11	.63
C ₆ H ₅ CH ₃69	Trace	Trace	.04
CH ₃ Cl.....	.39	.22	1.08	.57
C ₂ H ₃ Cl.....	.36	-	.07	1.98
C ₂ H ₅ Cl.....	1.13	.79	.54	1.28
(CH ₂ Cl) ₂54	-	-	3.08
Chloroprene.....	6.30	2.27	1.73	.71
Chlorobutene.....	.62	-	-	-
CH ₃ OH.....	-	-	.04	.19
C ₂ H ₅ OH.....	-	-	-	.30
i-C ₃ H ₇ OH.....	-	-	-	.06
n-C ₃ H ₇ OH.....	.27	(³)	-	-
CH ₃ CHO.....	-	.04	.04	2.61
(CH ₃) ₂ CO.....	.07	.07	.04	.49
HCOOH.....	-	-	.07	.08
CH ₃ COOH.....	2.39	-	-	-

¹ Material identification is given in table 1.

² Denotes hydrocarbons C₂ through C₄.

³ Unknown.

TABLE 5. - Products of neoprene compositions¹
(stagnation burner studies)

Product	Uncured, mg/g	Cured, mg/g	4A, mg/g	3A, mg/g
HC1.....	300.3	181.1	99.4	44.9
CO ₂	48.0	1,160	1,050	32.7
SO ₂95	6.36	5.74	.55
COS.....	-	.04	.03	.17
CS ₂	-	.01	.01	.54
H ₂ S.....	.05	.20	.06	.65
C _x H _y ²	3.53	7.44	4.60	1.91
C ₆ H ₆	1.42	.02	.10	.29
CH ₃ Cl.....	.51	.43	.37	.28
C ₂ H ₃ Cl.....	.38	-	.78	-
C ₂ H ₅ Cl.....	.55	.75	.78	.48
(CH ₂ Cl) ₂31	-	.04	3.32
Chloroprene.....	4.14	.26	.16	.83
Chlorobutene.....	4.07	-	-	-
CH ₃ OH.....	-	.26	-	.42
C ₂ H ₅ OH.....	-	-	1.50	-
i-C ₃ H ₇ OH.....	-	.05	-	-
n-C ₃ H ₇ OH.....	-	Trace	.17	.04
CH ₃ CHO.....	-	-	.08	5.29
(CH ₃) ₂ CO.....	.06	.01	.39	.99
HCOOH.....	-	-	Trace	-
CH ₃ COOH.....	.02	.01	.16	.80

¹ Material identification is given in table 1.

² Denotes hydrocarbons C₂ through C₄.

TABLE 6. - Products of PVC compositions¹
(sealed tube studies)

Product	PVC, mg/g	6A, mg/g	13A, mg/g	7A, mg/g	9B, mg/g	10B, mg/g
CO.....	19.7	4.84	5.02	5.65	8.91	5.83
CH ₄80	.20	.54	.55	.85	1.94
HC1.....	550.6	174.2	253.7	263.5	205.8	300.0
CO ₂	12.1	29.1	18.1	19.0	32.4	33.7
SO ₂38	.25	.37	-	-	.22
COS.....	-	.16	-	-	-	-
CS ₂	-	-	-	.36	-	-
C _x H _y ²	1.51	1.71	6.14	2.87	2.18	4.52
Isoprene.....	-	-	-	-	.66	-
C ₆ H ₆	47.5	5.12	26.7	25.4	35.8	19.5
Hexene.....	-	1.05	-	-	-	-
C ₆ H ₅ CH ₃61	.57	1.51	.84	.42	.58
C ₆ H ₄ (CH ₃) ₂08	.03	.08	.11	.02	.02
CH ₃ Cl1.....	.44	3.75	3.19	Trace	.72	.48
C ₂ H ₆ Cl.....	.05	-	-	.05	-	-
C ₂ H ₅ Cl1.....	.03	1.10	20.7	Trace	.34	.33
(CH ₂ Cl) ₂10	-	.81	-	-	-
Chloroprene.....	.56	.02	.19	-	-	.31
CH ₃ (CH ₂) ₄ CH ₂ Cl1.	.10	.16	-	.11	.35	-
C ₆ H ₅ CH ₂ Cl1.....	.03	-	-	Trace	-	-
CH ₃ OH.....	.03	.03	.05	.06	.05	.06
C ₂ H ₅ OH.....	.02	Trace	1.10	.28	4.88	.66
n-C ₃ H ₇ OH.....	.03	.23	.43	.02	1.18	1.11
i-C ₃ H ₇ OH.....	.07	-	Trace	.08	.40	.16
HCHO.....	(³)	.06				
CH ₃ CHO.....	.13	Trace	.02	.09	-	.02
(CH ₃) ₂ CO.....	.07	.64	.03	1.44	2.82	1.36
HCOOH.....	-	Trace	-	-	.16	.13
CH ₃ COOH.....	.06	.23	.30	.03	.72	.50

¹ Material identification is given in table 1.

² Denotes hydrocarbons C₂ through C₄.

³ Unknown.

TABLE 7. - Products of PVC compositions¹
(stagnation burner studies)

Product	PVC, mg/g	6A, mg/g	13A, mg/g	7A, mg/g	9B, mg/g
HCl.....	421.4	168.6	184.4	146.9	155.4
CO ₂	49.2	23.2	22.6	31.6	24.0
SO ₂23	.12	.40	-	-
COS.....	-	.11	-	-	-
C _x H _y ²	1.92	.65	3.03	.90	.33
C ₆ H ₆	39.4	16.0	33.3	17.6	32.0
Hexene.....	-	.73	-	-	-
C ₆ H ₅ CH ₃40	.48	.02	.09	.50
C ₆ H ₄ (CH ₃) ₂20	.02	Trace	Trace	Trace
CH ₃ Cl.....	.36	3.31	2.49	.51	.13
C ₂ H ₃ Cl.....	-	.16	.15	-	-
C ₂ H ₅ Cl.....	Trace	.50	12.4	.24	.03
CH ₃ (CH ₂) ₄ CH ₂ Cl.....	-	-	.05	-	2.11
C ₆ H ₅ CH ₂ Cl.....	-	.01	-	-	-
CH ₃ OH.....	.01	.03	.04	.03	.04
C ₂ H ₅ OH.....	-	Trace	7.22	.38	.05
n-C ₃ H ₇ OH.....	Trace	.04	.48	Trace	Trace
i-C ₃ H ₇ OH.....	.01	.02	.06	.01	Trace
HCHO.....	(³)				
CH ₃ CHO.....	.16	-	.77	-	-
(CH ₃) ₂ CO.....	.01	.15	.59	1.26	.02
HOOC.....	.10	-	-	-	-
CH ₃ COOH.....	.01	.04	.47	.38	.14
HC ₂ OOC ₂ H ₅	-	-	.56	.02	-
4-Methylcyclohexanone.....	-	-	-	-	2.08

¹Material identification is given in table 1.

²Denotes hydrocarbons C₂ through C₄.

³Unknown.

TABLE 8. - Products of urethane rigid foams¹
(sealed tube studies)

Product	Material 1B, mg/g	Material 2B, mg/g	Material 16A, mg/g
CO.....	-	-	34.5
CH ₄	1.60	0.96	2.36
HC1.....	23.2	5.85	17.3
NH ₃	3.17	10.7	-
HCN.....	Trace	Trace	Trace
CO ₂	144.2	148.7	191.5
C _x H _y ²	1.81	3.90	2.18
C ₆ H ₆	2.92	.77	.18
C ₆ H ₅ CH ₃21	.18	.30
CH ₃ Cl.....	1.08	1.03	.22
C ₂ H ₃ Cl.....	.28	.22	.22
C ₂ H ₅ Cl.....	11.70	7.43	.07
CH ₂ Cl-CH ₂ Cl.....	40.0	52.0	17.7
CH ₂ Cl-CH=CH ₂87	.51	.23
C ₆ H ₅ Cl.....	.14	.04	-
CH ₂ Cl-CH ₂ Br.....	-	-	26.0
CH ₃ Br.....	-	-	1.85
C ₂ H ₃ Br.....	-	-	.51
C ₂ H ₅ Br.....	-	-	3.12
CH ₂ Br-CH ₂ Br.....	-	-	12.5
CFC1 ₃	89.2	56.0	9.25
CHFC1 ₂	1.63	.92	-
CH ₃ OH.....	.02	.07	.44
C ₂ H ₅ OH.....	.42	.77	-
i-C ₃ H ₇ OH.....	.07	.07	Trace
n-C ₃ H ₇ OH.....	.03	-	Trace
CH ₂ Cl-CH ₂ OH.....	1.29	1.10	.03
CH ₂ Cl-CHOH-CH ₃94	2.91	3.41
CH ₃ CHO.....	-	-	.15
Sorbaldehyde.....	-	-	1.04
(CH ₃) ₂ CO.....	2.37	1.54	14.4
CH ₃ COCH ₂ H ₅50	.74	.16
1,4-Dioxane.....	.14	.18	1.67
HCOOH.....	-	.06	.04
CH ₃ COOH.....	.02	.39	1.52
C ₆ H ₅ NH ₂	58.6	66.9	-
p-Toluidine.....	10.3	7.4	-
p-Phenylenediamine.....	(³)	Yes	-
2,4-Toluenediamine.....	(³)	Yes	-

¹ Material identification is given in table 1.

² Denotes hydrocarbons C₂ through C₄.

³ Unknown.

TABLE 9. - Products of pine samples¹
(sealed tube studies)

Product	Untreated pine 1D, mg/g	Untreated pine 6D, mg/g	Treated pine 2D, mg/g	Treated pine 3D, mg/g	Treated pine 4D, mg/g	Treated pine 5D, mg/g
H ₂	0.09	0.07	0.13	0.01	0.01	0.13
CO.....	48.1	48.3	45.1	20.7	58.1	43.4
CH ₄	2.21	.78	1.18	2.79	.98	2.30
H ₂ O.....	324.8	276.6	268.1	243.1	306.3	320.2
HC1.....	19.3	-	.51	-	-	-
HCN.....	(³)	(³)	(³)	(³)	.51	(³)
CO ₂	112.1	115.8	73.8	77.7	88.7	135.4
SO ₂	-	-	-	-	15.0	-
COS.....	-	-	-	-	.08	-
C _x H _y ²39	.85	1.22	1.03	1.04	.36
C ₆ H ₆57	.28	.82	.92	1.43	.50
C ₆ H ₅ CH ₃11	.54	5.64	17.7	.29	.25
Xylenes.....	.05	.02	.18	.04	-	Trace
CH ₃ Cl.....	-	-	3.41	.11	-	.05
C ₂ H ₅ Cl.....	-	-	-	.03	-	-
CH ₃ OH.....	13.8	7.74	5.15	6.48	9.42	7.97
HCHO.....	1.85	2.38	1.84	1.68	3.64	2.40
CH ₃ CHO.....	1.22	1.54	3.57	.43	.07	1.21
Furfural.....	1.56	2.18	3.04	4.32	1.39	4.28
5-Methyl-2-furaldehyde.....	.07	.03	.01	.02	-	.02
Acrolein.....	.67	.62	1.21	.43	(³)	.47
(CH ₃) ₂ CO.....	1.38	3.15	1.77	2.72	2.01	1.49
CH ₃ COC ₂ H ₅44	1.34	.36	1.19	1.24	.86
CH ₃ COC ₃ H ₅	2.70	1.83	.56	2.75	.02	.35
2,3-Pentanedione.....	.11	.10	.29	.30	-	-
HCOOH.....	(³)	(³)	(³)	(³)	.23	(³)
CH ₃ COOH.....	7.74	7.27	7.68	10.9	-	4.57
Methyl formate.....	4.24	2.78	5.44	2.32	.93	.84
Methyl acetate.....	2.63	1.84	2.08	1.95	3.96	.88
Vinyl acetate.....	2.11	2.28	2.02	1.37	.08	.18
Furan.....	1.15	1.46	2.83	1.13	.36	1.60
2-Methylfuran.....	1.19	2.13	1.23	.32	.35	2.13
2,5-Dimethylfuran....	.60	.40	.27	3.38	.13	.84

¹ Material identification is given in table 1.

² Denotes hydrocarbons C₂ through C₄.

³ Unknown.

TABLE 10. - Products of pine samples¹
(stagnation burner
studies)

Product	Untreated pine 1D, mg/g	Treated pine 2D, mg/g	Treated pine 3D, mg/g	Treated pine 4D, mg/g	Treated pine 5D, mg/g
H ₂ O.....	486.2	334.3	224.3	468.5	410.3
HC1.....	1.46	8.57	-	-	-
CO ₂	199.6	226.8	171.8	274.0	590.9
SO ₂	-	-	-	22.3	-
COS.....	-	-	-	.12	-
HCN.....	(³)	(³)	(³)	1.32	(³)
C _x H _y ²85	1.37	.59	.87	1.53
C ₆ H ₆86	.85	1.61	1.08	.19
C ₈ H ₅ CH ₃07	20.0	22.0	.03	.19
Xylenes.....	Trace	Trace	-	.03	.01
CH ₃ Cl.....	.22	.46	.30	-	-
CH ₃ OH.....	2.78	4.15	3.68	8.81	5.17
HCHO.....	2.09	.37	.71	.50	9.97
CH ₃ CHO.....	2.53	.84	.81	.76	1.12
Furfural.....	1.09	1.15	2.23	4.85	3.18
5-Methyl-2-furaldehyde.....	Trace	Trace	-	Trace	-
Acrolein.....	.21	.70	.59	.22	.68
(CH ₃) ₂ CO.....	2.81	2.02	1.80	.45	1.45
CH ₃ COC ₂ H ₅69	.15	.62	.48	.70
CH ₃ COC ₃ H ₅71	1.74	1.55	-	.52
2,3-Pentanedione.....	Trace	Trace	-	-	.04
HCOOH.....	(³)	(³)	(³)	.13	(³)
CH ₃ COOH.....	.01	.62	3.04	.30	2.83
Methyl formate.....	.28	1.23	1.12	.04	.23
Methyl acetate.....	.76	.96	.85	.45	.18
Vinyl acetate.....	1.48	1.76	1.90	.06	.16
Furan.....	1.41	.88	1.26	.37	.79
2-Methylfuran.....	1.05	1.77	1.06	.06	.76
2,5-Dimethylfuran.....	.79	1.62	.96	.03	.18

¹ Material identification is given in table 1.

² Denotes hydrocarbons C₂ through C₄.

³ Unknown.

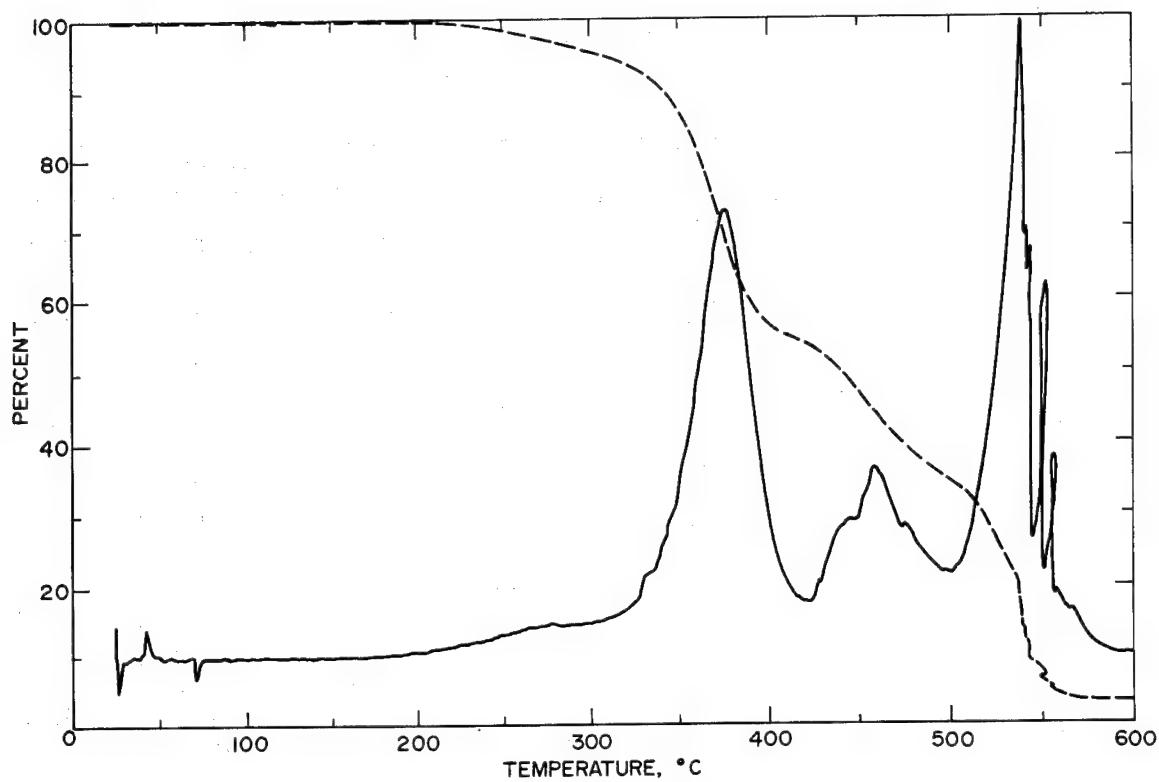


FIGURE 4. - TGA of uncured neoprene.

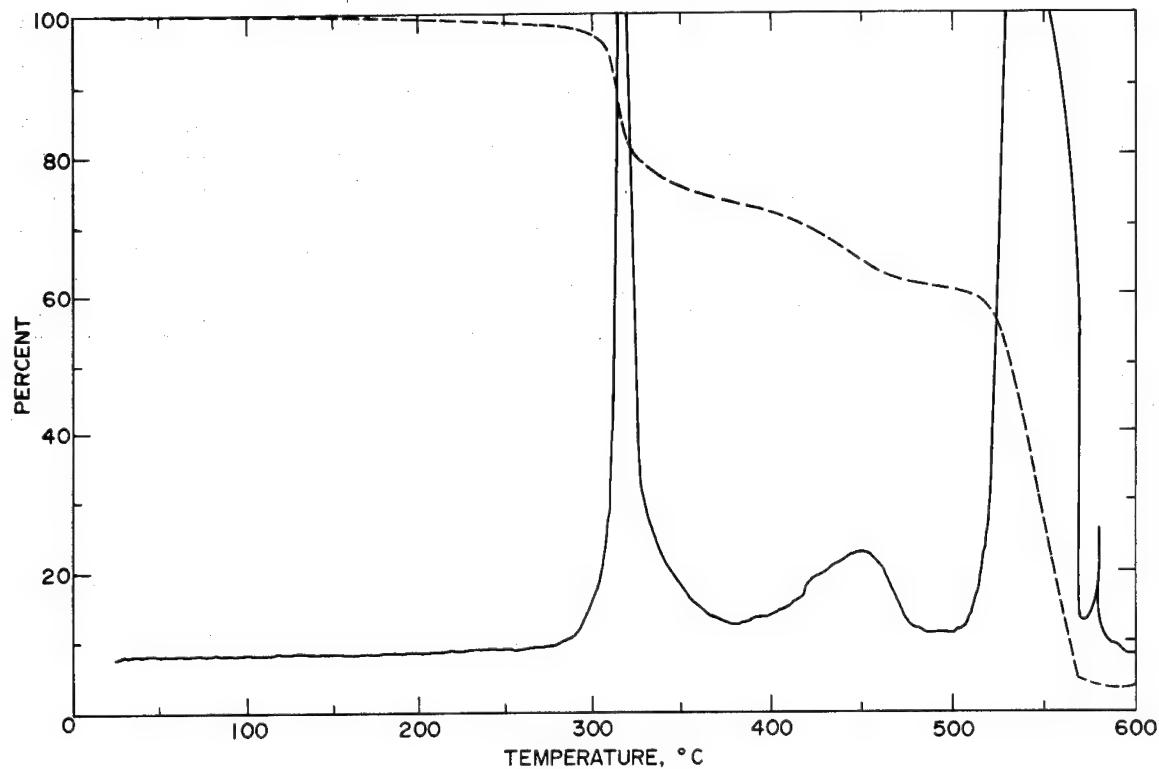


FIGURE 5. - TGA of known composition cured neoprene.

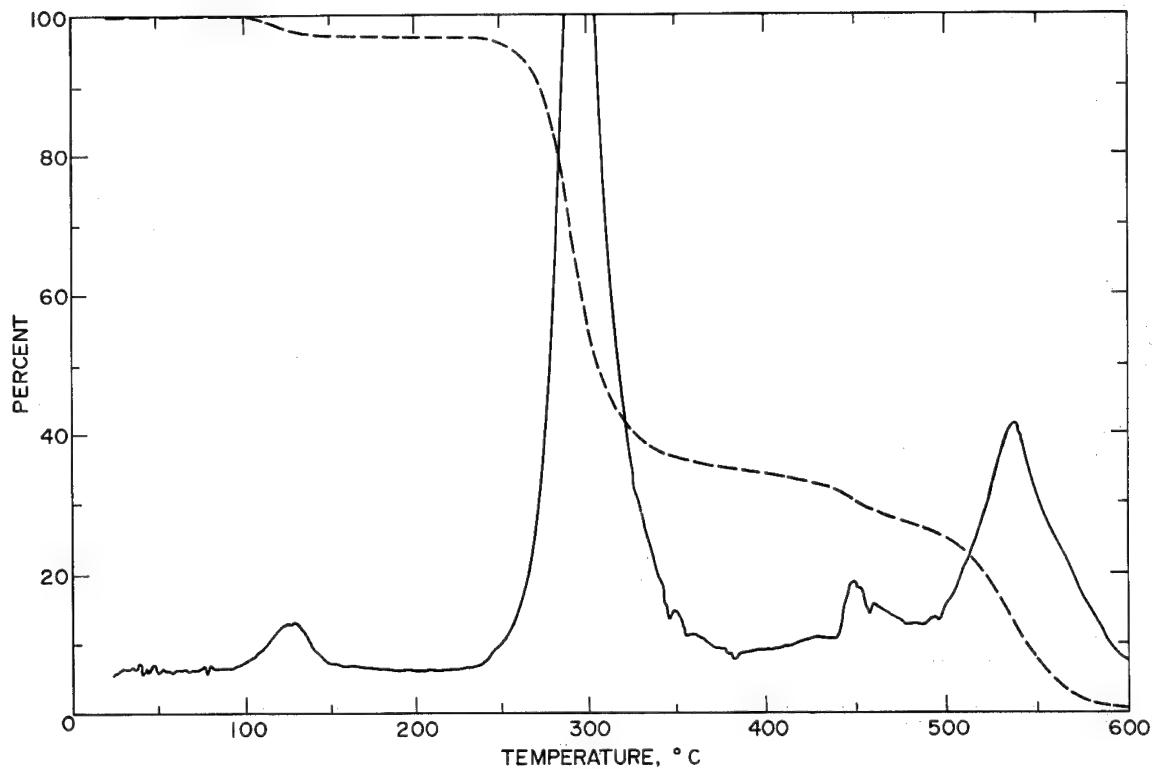


FIGURE 6. - TGA of "pure" polyvinyl chloride resin.

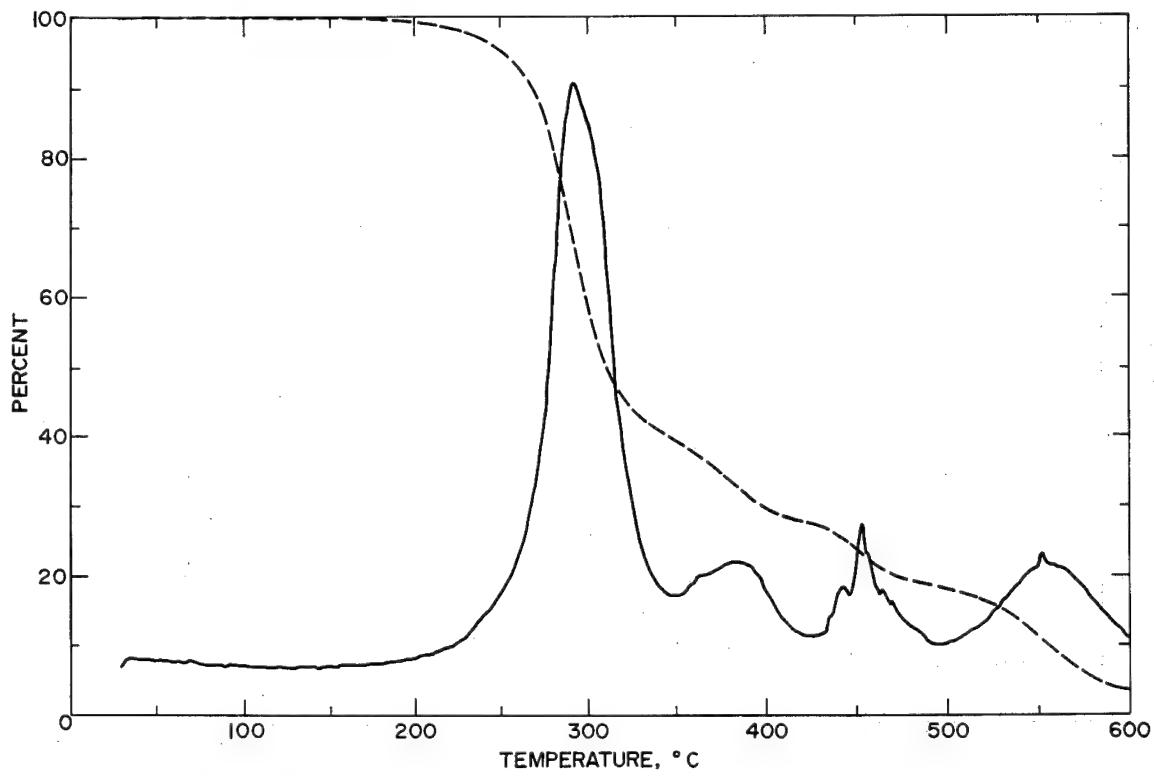


FIGURE 7. - TGA of polyvinyl chloride composition 13A.

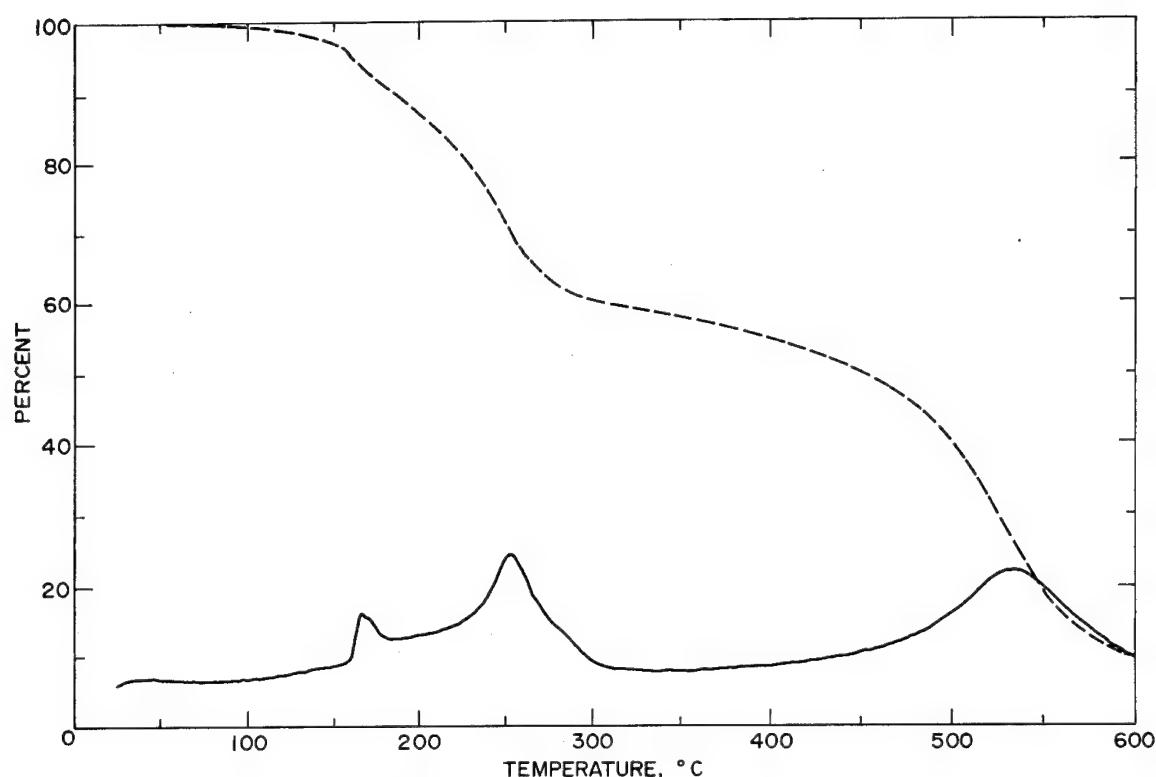


FIGURE 8. - TGA of urethane foam material 2B.

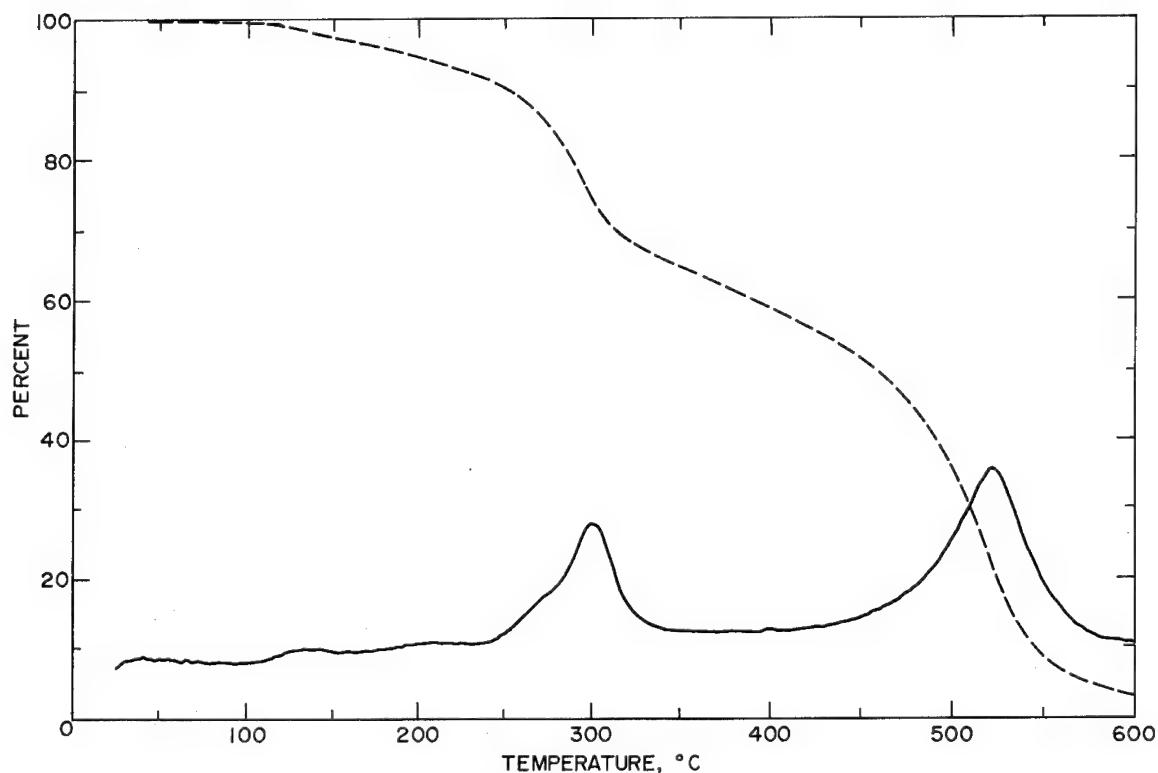


FIGURE 9. - TGA of urethane foam material 16A.

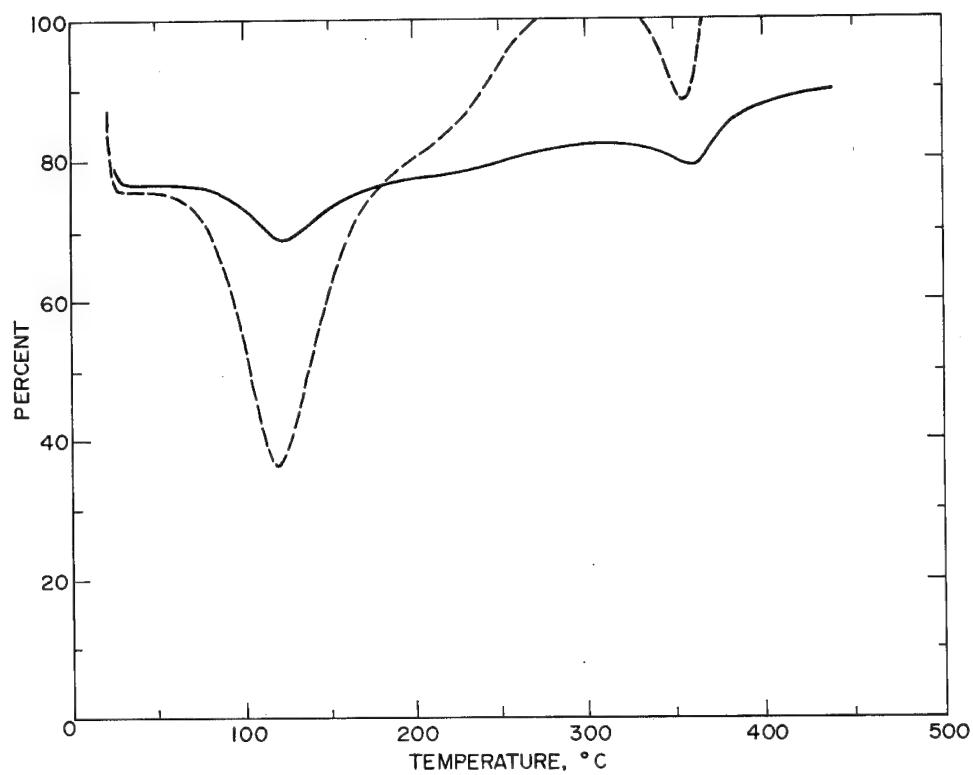


FIGURE 10. - DTA of untreated standard southern yellow pine
(material 6D).

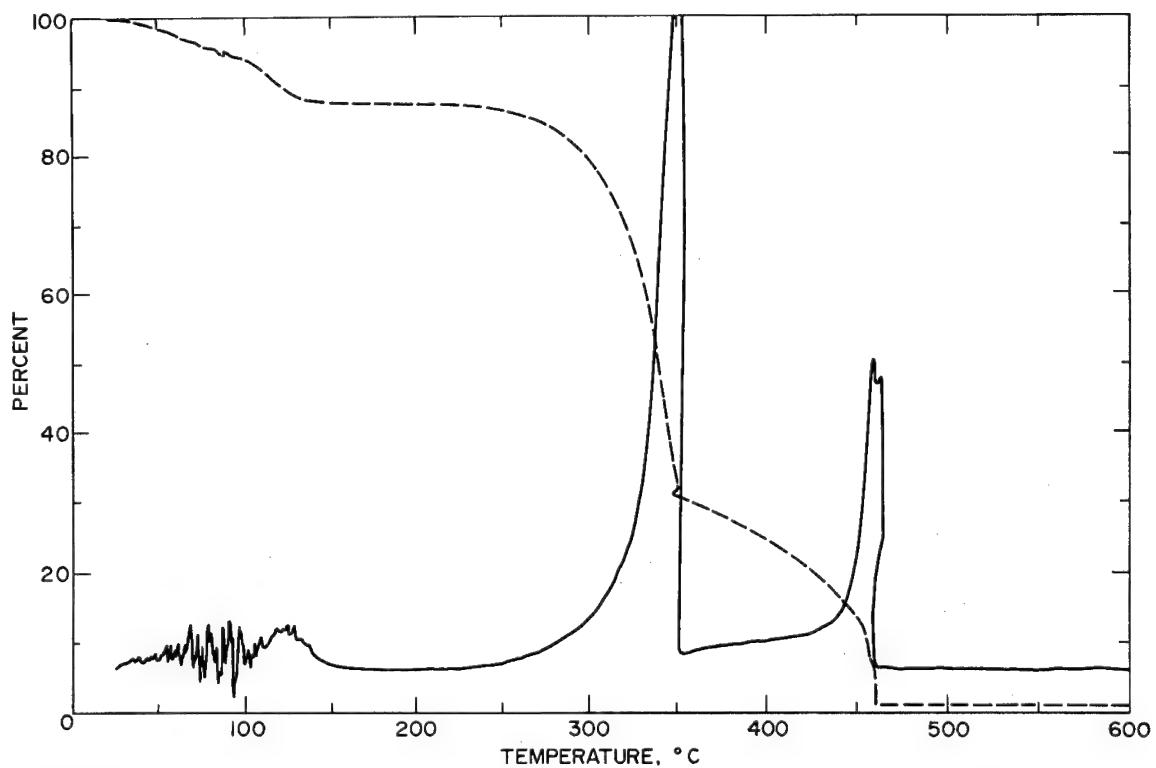


FIGURE 11. - TGA of untreated standard southern yellow pine (material 6D).

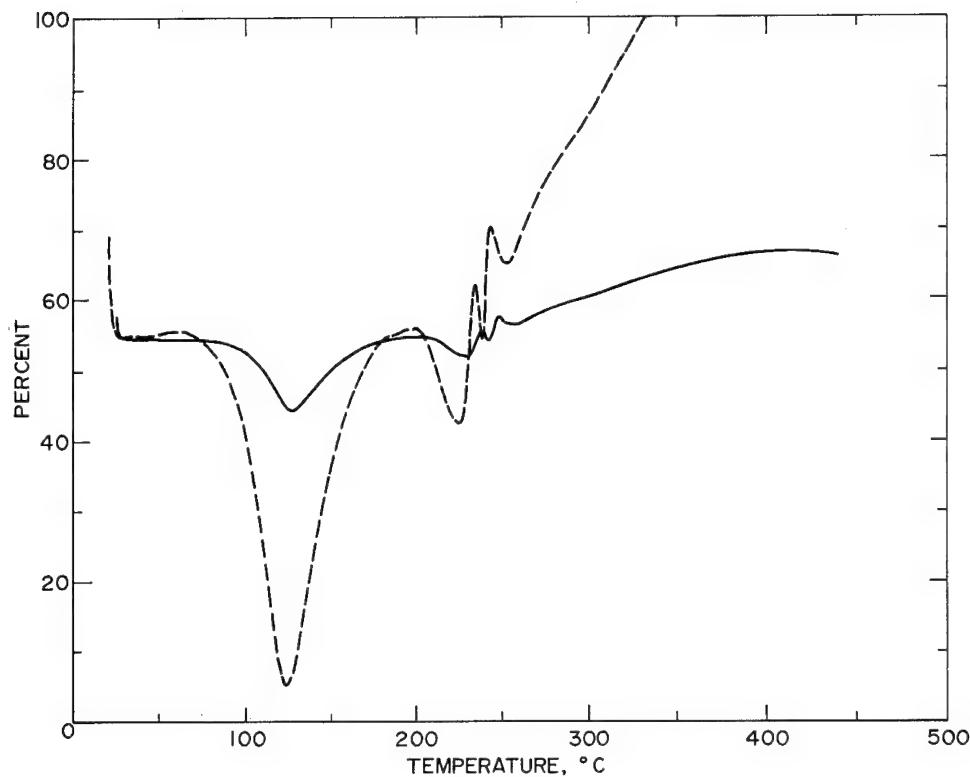


FIGURE 12. - DTA of Minalith-treated standard southern yellow pine (material 4D).

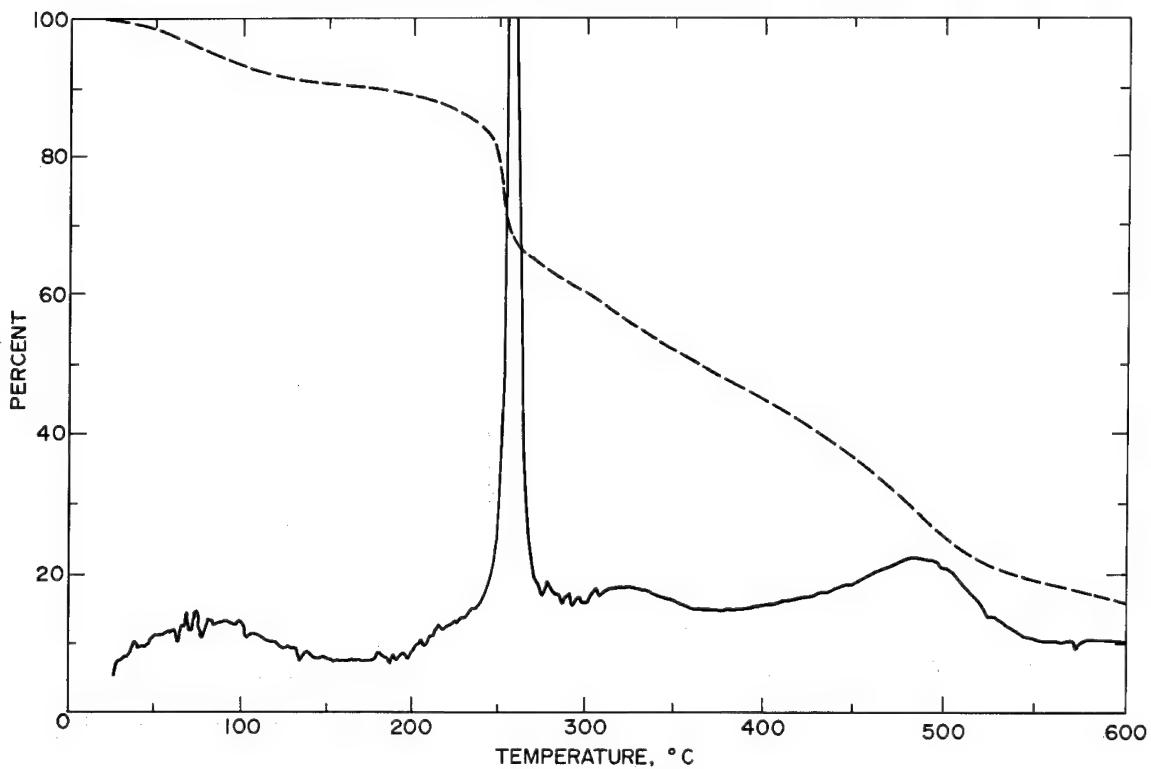


FIGURE 13. - TGA of Minalith-treated standard southern yellow pine (material 4D).

Neoprenes

Four neoprene compositions were studied: Neoprene gum, known cured neoprene (the composition of which is given in table 11), and two neoprene rubbers from actual hose conduits used in mining applications. The TGA curves for these four materials clearly show that the cured compositions start to decompose at a lower temperature and have a faster decomposition rate than the raw gum, indicating that vulcanization lowers the thermal stability of neoprene. Significantly, the material loss as emphasized by the TGA derivative curve appears to correspond fairly closely to the quantity of hydrogen chloride liberated, with the exception of material 3A (table 12). This finding is not surprising, since decomposition of the polyester reinforcement was most likely responsible for the additional initial weight loss observed.

TABLE 11. - Composition of cured neoprene

Name	Ingredient description	Pct
Neoprene WRT.....	Poly 2-chlorobutadiene 1,3 (Du Pont).....	62.50
Neozone A.....	N-phenyl-alpha-naphthylamine (Du Pont).....	1.25
Wecoline 300.....	Distilled stearic acid (Drew Chemical Corp.).....	.31
Maglite Y.....	Magnesium oxide (Merck and Co.).....	1.25
NA-22.....	2-mercaptopimidazoline (Du Pont).....	.31
Protox-166.....	Zinc oxide surface treated with propionic acid (The New Jersey Zinc Co.).	3.13
ISAF.....	Intermediate superabrasion oil furnace black (J. M. Huber Corp.).	31.25

TABLE 12. - Comparison of chlorine content values as obtained by different means for neoprene compositions

Sample	HCl found, pct		Weight loss, pct TGA	Theory, pct
	Sealed system	Stagnation burner		
Uncured neoprene.....	31.2	30.0	32.0	41.24
Known cured neoprene.....	20.0	18.1	19.0	25.78
Composition 4A.....	11.0	9.9	10.0 or 12.3	-
Composition 3A.....	6.5	4.5	11.3 or 16.3	-

As evident from the data presented in tables 2 and 3, the cured compositions did consume more oxygen than the raw gum. Another aspect worth noting is that under dynamic conditions two of the vulcanized materials glowed. The glow occurrence was reflected in the tenfold increase in the carbon dioxide production (compare tables 4 and 5), and also increased sulfur dioxide (TLV,⁷ 5 ppm) and carbonyl sulfide formation. Under the milder sealed tube (static) conditions, carbon disulfide (TLV, 20 ppm) and hydrogen sulfide (TLV, 10 ppm) were the major sulfur-containing species identified and quantitated. The sulfur-containing species are derived from polymerization initiators, antioxidants, and curing agents. Trace quantities of formaldehyde, substituted

⁷Threshold limit value, American Conference of Governmental Industrial Hygienists.

phenols, cresols, benzyl chloride, chlorinated aromatics, alkyl substituted aromatics, and mercaptans were detected.

The main toxic product obtained from neoprene-type compositions is hydrogen chloride (TLV, 5 ppm) formed at 370° C in 76 pct yield from uncured neoprene based on the chlorine content. Minor, but nevertheless important, products found are SO₂ (TLV, 5 ppm), CS₂ (TLV, 20 ppm), H₂S (TLV, 20 ppm), CO (TLV, 50 ppm), benzene (TLV, 25 ppm), chloroprene (TLV, 25 ppm), and the various mercaptans (TLV, 0.5 ppm) that were detected but not quantitated under the Ultrasystems' contract.⁸ Other water-soluble toxic materials, namely acetic (TLV, 10 ppm) and formic acids (TLV, 5 ppm), were also detected and quantitated.

Polyvinyl Chloride Compositions

Six polyvinyl chloride compositions were investigated. Tables 6-7 compile the identified and quantitated products of the degradations performed on the studied PVC compositions. Comparing tables 6-7, it is apparent that no large differences exist between the product mix obtained under static and dynamic conditions. This is not surprising since no glow occurred in the stagnation burner tests. The three main volatiles found in the virgin PVC resin investigations were hydrogen chloride, carbon monoxide, and benzene. However, the other compositions afforded a variety of products. Thus, in the case of material 6A, benzene no longer was the main hydrocarbon products; in fact, the amount found was lower than would be deduced from the evolved hydrogen chloride assuming the latter to be derived from the PVC component only. On the other hand, the methyl chloride produced was about an order of magnitude higher than in the pure PVC. These findings tend to indicate that the relative quantity of species derived from a given composition component; for example, PVC resin itself is dependent on the nature of the other materials present in the composition. It can be speculated that toxic product formed from compounded material is not necessarily the sum of toxic products of the pure constituents. Mass spectral analysis indicates the presence of benzyl chloride (TLV, 1 ppm).

In the static studies of PVC compositions, the oils were found to consist of a mixture of phthalate esters and phthalic anhydride, whereas in the dynamic studies mainly the phthalate esters were observed. This would tend to indicate that under the flow conditions, the plasticizer evaporates mostly unchanged and is immediately swept out of the reaction zone; being exposed to heat for a considerable period of time in the static system, the plasticizer undergoes transformation to phthalic anhydride and other products. No oils were found in the case of pure PVC resin, which is to be expected since no plasticizer was present.

Comparing the data given in tables 6-7 for the various PVC compositions, it is obvious that production of chlorinated organic species is not necessarily dependent upon the material's PVC content (assuming that hydrogen chloride is derived only from the PVC component and that no other chlorinated compounds

⁸Work cited in footnote 4.

are present). Thus, in material 7A, the ethyl chloride produced is much higher than can be deduced from its PVC content; the same applies to methyl chloride production in the compositions 6A and 13A. Consequently, the data obtained from a given pure composition insofar as the nature and relative product concentration is concerned, can be used only as a guideline regarding the expected production of individual species from a composite.

For the polyvinyl chloride compositions, the main toxic species is undoubtedly hydrogen chloride and not CO; this is presumably due to the relatively low temperatures involved. Other important components are benzene, phthalates, the aldehydes, and carbon monoxide. Although under these conditions CO does not seem to pose a great danger, this does not mean that the same applies to fire condition wherein the temperatures involved are significantly higher. Previous work⁹ has demonstrated that CO production increases with temperature. Benzene (TLV, 25 ppm), which is produced in a larger quantity than carbon monoxide (TLV, 50 ppm), may represent a greater hazard at relatively low temperatures.

The TGA curves obtained for the polyvinyl chloride compositions have a characteristic trace. This is due to the evolution of hydrogen chloride that occurs just beyond 250° C. In contrast to the neoprene investigations, there was no correlation between the first peak and the quantity of hydrogen chloride evolved from PVC compositions with the exception of the pure resin.

Urethane Foams

The urethane foam investigation was confined to two, composition 1B, 2B (1B and 2B are essentially identical), and 16A. The foams were studied only in the static system since their low weight/volume ratio made them unsuitable for stagnation burner testing. Table 8 compiles the products detected and quantitated on a milligrams-per-gram basis. Based on the types and the quantities of volatile halogenated products, it would appear that volatile halogenated products originate in all three foam samples from a halogenated organic compound. Foams 1B and 2B contain a chlorinated organic constituent, and in foam 16A, the organic constituent contains bromine in addition to chlorine. The aforementioned becomes particularly apparent (table 8) when the quantities of 1,2-dichloroethane formed from foams 1B and 2B are compared with the quantities of 1,2-dichloro-, 1-chloro-2-bromo-, and 1,2-dibromoethane produced during decomposition of foam 16A. These ingredients are most likely responsible for the formation of the highly toxic chloroethanol (TLV, 5 ppm) and chloropropanol. Other differences between the foams are in the production of ammonia and the aromatic amino compounds, aniline (TLV, 5 ppm), p-toluidine, p-phenylenediamine, and 2,4-toluene diamine from materials 1B and 2B, whereas none were found for the urethane 16B. Carbon monoxide was detected only from decomposition of material 16B. Traces of cyanide and isocyanate were found in all three foams. It can be safely stated that in the 1B and 2B urethane system, aniline was the major toxic component, whereas in the composition 16A, carbon monoxide appeared to be the major toxic product found.

⁹Work cited in footnote 5.

Woods

In this area, the investigation was limited to untreated and variously impregnated samples of standard southern yellow pine; these are listed in table 1. The impregnations were performed by Koppers Co., Pittsburgh, Pa., and are standard procedures described by the American Wood-Preservers' Association. The products detected and quantitated are presented in tables 9-10. Of all the treatments, the one involving Minalith (flame retardant) had the most pronounced action on the thermal oxidative degradation of the wood as evidenced by DTA and TGA curves, and the relatively high char yield and the low tar production (under the stagnation burner conditions; table 3). It is evident (table 3) that low char or residue resulted when glow occurred. The Minalith treatment also changed significantly the nature and relative concentration of the products formed. This is shown by the formation of SO_2 , COS, HCN, which were not formed by any of the other woods, and the increased quantity of carbon monoxide (tables 9-10). The other treatments, pentachlorophenol, cresote, and CCA, failed to make a significant change in the products; exceptions were the formation of hydrogen chloride and methyl chloride in the case of pentachlorophenol and the relatively large concentration of toluene found in the cresote and pentachlorophenol-impregnated woods. The large concentration of toluene is most likely associated with the use of an oil impregnation medium. None of the treatments did seem to alter the production of the typical wood toxic species such as formaldehyde, acrolein, furfural, and formic acid.

SUMMARY

Organic materials such as conveyor belts, brattice cloths, or wood evolve toxic products when subjected to elevated temperatures or when involved in a fire. Used in underground mines, these items can therefore create health and safety problems, which for the well-being of mining personnel must be defined in order to provide acceptable solutions.

Accordingly, the Bureau of Mines initiated this program to determine the severity of the problem with the ultimate objective to supply mine operators and mine inspectors with quantitative data that will make it possible to establish fairly safe operating procedures. The approaches taken under this program have proceeded along four lines: (1) To determine the nature and the quantity, on a gram per gram basis, of all decomposition products formed by finished articles and by the individual components of finished articles; (2) to investigate the possibility of improving materials used in mines at reasonable costs, so that less flammable materials could be developed that also will form less toxic products upon decomposition; (3) to develop routine testing procedures to insure that no obviously inferior materials are introduced into mines; and (4) to establish those quantities of materials that can be used with a minimum of risk in a given location under specific conditions, such as predetermined ventilation airflow rate.

The specific compositions studied in detail under this program are polyvinyl chloride-based materials such as brattice cloth and ventilation pipe, neoprene-based items such as hose conduit and trailing cable insulation, rigid

urethane foams, and variously treated samples of southern yellow pine. The results obtained to date tend to indicate that the types and relative quantities of specific decomposition products formed from finished items are not necessarily predictable from the decomposition behavior of the individual components. It also was established that the toxicological hazards of materials used for the same function, for example, cable insulation, can differ by factors of two and more, which in turn means that hazards can be reduced by selecting the proper material. A further outcome of the work is the development of more sensitive and accurate analytical procedures.

Future efforts will be concerned with testing of additional materials, gaining a better understanding of the effects one component has on the decomposition behavior of another, the development of routine, yet reliable decomposition and analysis procedures, and finally, establishing guidelines for material improvements and for safer use of finished articles. The results of this program will insure that the hazards to miners arising from decomposing organic materials will be reduced to a practical minimum and will provide mine operators and mine inspectors with the tools necessary to keep all risks at the lowest possible achievable level.